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INFORMATIVE SUMMARY WITH CONCLUSIONS

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Based on the known properties of DOWTHERM A and its use pattern, an analysis of the potential impact of this heat exchange fluid on the environment was made. The results would indicate that its present use will tolerate a slow leak (25 lbs/day) into a stream which has a minimum flow rate of approximately 200 cubic feet/second. Fail safe conditions should be installed at the site to prevent accidental spills of large quantities into the stream.

Characteristics of this product including biodegradability and a sufficiently low partition coefficient to preclude bioaccumulation suggest that it is a safe ecological material when used appropriately. The ecological hazard that may be incurred with DOWTHERM A appears to be much smaller than that incurred with polychlorinated biphenyls. In view of these findings and a demand for a replacement for the PCBs we recommend that the following work be undertaken.

1. Establish the movement of this material in the environment experimentally.

2. Study the metabolism and accumulation pattern of DOWTHERM A in aquatic speices and compare it with PCB.

Further recommendations are made in the report.

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DOWTHERM® A AND THE ENVIRONMENT

INTRODUCTION

DOWTHERM® A, a eutectic mixture of diphenyl (DP) and diphenyl oxide (DPO), is an industrial heat transfer agent. Cu rently, there is considerable pressure to discontinue the use the principal competitor, the polychlorinated biphenyls (PCBs Because the use of PCBs is under fire[1] questions concerning t environmental hazards that may be incurred with the use of DO THERM A are being asked. The purposes of this report are as follows: 1. to develop a model which may aid in integrating data and predicting the environmental hazard, 2. to summariz the available data relevant to answering these questions, and 3. to suggest additional studies which are needed to support continued use of DOWTHERM A.

I. THE ENVIRONMENTAL QUESTIONS

The questions were of two types: 1) what is the effect of a shock load on a river? This may occur when several thousand gallons are accidentally dumped into a river. 2) the second question concerns the environmental impact of a slow leak into a river.

In analyzing the slow leak problem further, the following picture emerges.[2] A typical system uses 90,000 pounds. The loss from such a system as indicated by the make up sold to a customer amounts to 9,000 pounds/year. Assuming that all is lost to a river, 25 lbs/day would enter the river.

For a river flow of 300 cubic feet/second (minimum flow of Tittabawassee) to 800 cubic feet/second the following calculations can be made:

300 cu ft/sec = 200 $\overline{M}$ gallons/day = 1660 $\overline{M}$ lbs/day
This flow will dilute 25 lbs to 0.015 ppm by weight.

800 cu ft/sec will dilute 25 lbs to 0.0062 ppm by weight.

Obviously, the magnitude of any chronic problem will be intimately associated with the characteristics of the water system near the location.

II. THE MODEL

Once DOWTHERM A enters the stream partitioning between the three major sinks; air, water, and soil, takes place. A useful model to describe the fate of a chemical is shown in the following equation (1).

$$
\begin{tikzcd}
 & & \text{Exchangeable Air Compartments} \arrow[d, shift left] & & \\
 & & \text{Air} \arrow[u, shift left] \arrow[rr] \arrow[dl, shift left] \arrow[dr, shift left] & & \text{Air Sink} \\
\text{Water Sink} & \text{Water} \arrow[l] \arrow[ur, shift left] \arrow[rr, shift left] \arrow[d, shift left] & & \text{Soil} \arrow[ul, shift left] \arrow[ll, shift left] \arrow[r] \arrow[d, shift left] & \text{Soil Sink} \\
 & \text{Exchangeable Water Compartments} \arrow[u, shift left] & & \text{Exchangeable Water Compartments} \arrow[u, shift left] &
\end{tikzcd} \qquad (1
$$

In this equation, it is assumed that exchange and equilibrations of an agent occurs between three major compartments shown at the vertices of the triangle--air, water, and soil. The chemical may exit these compartments by physical or chemical deactivation. This is represented by a one-way arrow from the major compartments into a sink. Of course, it should be recognized that the single sink indicated in Equation 1 for deactivation may represent multiple methods for deactivation. The exchangeable compartments in air, water, and soil represent exchanges between different components within the major compartments. For example, exchanges between different types of soil, exchanges between particles suspended in either air or water. These exchangeable compartments may be and are very likely to be numerous.

The next section will collect together the known properties of DOWTHERM A which will be matched to this model. This will allow an evaluation of the need for additional data.

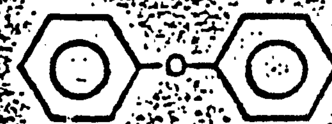
III. SUMMARY OF AVAILABLE DATA

A. Chemical and Physical Properties

DOWTHERM A is a eutectic mixture of diphenyl (26-27%) and diphenyl oxide (73-74%). The hand sheets prepared by the Thermal Laboratory provide the following information for these compounds.

TABLE I

Chemical and Physical Properties of DOWTHERM A

Parameter	Diphenyl	Diphenyloxide
Structure		
b.p.	255°	258°
m.p.	69°	27°
Density @25°C	1.156	1.07
v.p. @25°C	9.75×10^{-3} mm Hg	1.87×10^{-2} mm
Solubility @25°C Water	75 ppm	21 ppm
n-Hept	112 g/100	infinite
log Partition Coef. octanol/water*	4.07	4.21
Mol wt.	1154	170

*Determined by the Analytical Laboratory.

In addition to the above, a letter[3] from W. E. Wass of Waste Control Engineering to S. Putman on October 13, 1965, has some useful data. In an aeration experiment 200 cc air/min/liter of solution was passed over a 20.5 ppm of DOWTHERM A. The results indicate that 68% is removed in 1 hour and 93% is removed in 4 hours.

B. Biological Properties

1. Aquatic Organisms. The toxicity of DOWTHERM A to aquatic species was evaluated by the Bionomics Laboratory in Wareham, Mass.[4] and is summarized in Table II.

TABLE II

Toxicity of DOWTHERM A in Aquatic Species

Species	TL50 (48 hours) Conc., ppm	No Effect Conc., ppm	No Effect Exposure Hours
Trout	2.7	1.6	120
Bluegill	2.1	1.1	120
Stickleback	1.4	0.7	120
Fathead Minnows	3.2	1.8	144
Scud* (static test)	0.04	0.02	48

*Scud is an anthropod similar to Daphnia.

Berg, et al.[5] analyzed homogenized tissues of an eviserated carp for DOWTHERM A. They reported a concentration of 110 ppm. Unfortunately, the authors did not indicate the environment from which the fish were sampled, the number of carp which were included in the evaluation, or the range of concentrations found. If it is assumed that the concentration of DOWTHERM A in the water was below the TL_{50} reported in Table II than Berg's results suggest a potential magnification factor. This observation needs to be explored in greater depth.

2. Mammalian Toxicity and Metabolism. The single dose oral toxicity of DOWTHERM A is low. All rats given 6 g/kg died while none of the rats given 2 g/kg died.[6] The cummulative toxicity appears to be low because rats survived 132 daily doses of 1 g/kg or 0.5 g/kg. This suggests that the compound must be fairly rapidly excreted.

Slight to moderate changes were observed in the histological structure of the kidneys, livers, and spleens of rats given 1 g/kg/day. Similar changes were not observed in rats receiving 0.5 g/kg/day. Decreased weight gains and increased liver and kidney weights were observed in both groups.[6]

The finding that 64% of a single dose, 1 g/kg, is excreted within 4 days following administration supports the conclusion that DOWTHERM A is not markedly accumulated in the body.[7] Free phenolic compounds and phenols conjugated with glucuronide accounted for 24 and 26 percent of that excreted respectively.

It should be emphasized that neither the toxicology studies or the metabolism study can be used as definitive evidence that DP or DPO does not accumulate in fat. DDT has a low order of accumulative toxicity and approximately 70% of an administered dose is eliminated within a few days. The portion of DDT which is retained is located primarily in the fat and is excreted slowly. None of the reported metabolism studies of DOWTHERM A include a material balance evaluation. Therefore, the 30-40% which has not been accounted for in existing studies may be located in the fat or other compartments of the body. The clearance from these pools may be very slow.

3. Biological Oxygen Demand (BOD) and Carbon Oxygen Demand (COD) of DOWTHERM A.[8] In considering the environmental hazard of DOWTHERM A, it is important to determine whether it is degradable in the environment. Data supporting the degradability of DOWTHERM A in the environment are as follows: 1. The BOD for diphenyl after 5, 10, and 20 days incubation were 0.08, 2.13, and 2.33 respectively. Theoretically, the BOD for this compound would be 3.01

2. The BOD for diphenyl oxide at the same time intervals were 2.00 2.01, and 2.16 respectively. Theoretically, the BOD for diphenyl oxide would be 2.64. 3. The COD for diphenyl oxide after 10 days of incubation is 2.19 while the theoretical COD is 2.64.

The BOD values for diphenyl and diphenyl oxide and the COD value for diphenyl oxide suggest that these compounds are susceptible to oxidation (degradation) by bacteria and by dichromate. In the case of diphenyl the low value after 5 days of incubation and a subsequent high value after 10 days suggests that bacteria may be induced to more efficiently oxidize diphenyl.

4. Screening Data. Screening data indicate the DP and DPO have either no or minimal activity on a variety of plant and insect species. A saturated solution of DP or DPO inhibits the growth of some species of bacteria--*S. aureus*, *A. niger*, and *A. terreus*.

5. Other Data for Assessing the Fate of DOWTHERM A in the Environment. The following information characterizing the biodegradability of DOWTHERM A has been reported:[10]

1. Twenty-eight days after preparing a system (closed to the air) containing 10 ppm DOWTHERM A and nonsterile Kawkawlin loamy soil, 0.2% of the diphenyl and 23% of the diphenyl oxide remained. In this case, it appears that diphenyl was more susceptible to degradation. Since only 68% and 57% of the diphenyl oxide and diphenyl were recoverable immediately following mixing, it appears that these agents are tenaciously bound to components of the soil.

2. No DOWTHERM A was recovered after 66 hours of incubation from a closed system which initially contained a 1:20 dilution of aromatic acclimated sludge and 50 ppm DOWTHERM A.

3. Within 48 hours, a species of Pseudomonas isolated from the Dow phenol return sludge degraded all of the DOWTHERM A in a closed system which initially contained 100 ppm DOWTHERM A. The diphenyl oxide disappeared faster than diphenyl.

4. No significant loss of DOWTHERM A occurred in a system containing Tittabawassee river water collected above the plant

bacterial count, 1 x 10^4/ml, in (did not change during the incubation. However, the type of organisms changed suggesting that DOWTHERM A selectively inhibits certain bacteria. After 5 days of incubation, 20% of the diphenyl oxide and 35% diphenyl were recovered from a closed system containing nonsterile bottom sediment obtained from the Titabawassee River above the plant site and 50 ppm DOWTHERM A. The proportion of the loss which may have been caused by binding to the sediment was not determined.

The information summarized above indicates that DOWTHERM A is degradable and suggests the ability of a system to degrade DOWTHERM A may be induced. Preliminary evidence suggests that a naive inoculum may take up to a month to acclimate sufficiently to significantly degrade DOWTHERM A.[11] In addition to degradation, binding to components of soil contributes to the loss of DOWTHERM A from various systems. The steady state level of such binding has not been determined. It was found that a portion of the DOWTHERM A bound to soil can not be extracted with hexane. Whether all of the DOWTHERM A bound to soil can be removed or whether it is susceptible to bacterial attack is unknown.

Within 24 hours, DOWTHERM A disappeared from an open system containing either sterile or nonsterile water and 20 ppm DOWTHERM A. This suggests that DOWTHERM A in an aqueous environment quickly volatilizes. Therefore, it may be important to determine the UV degradation of DOWTHERM A.

IV. RESULTS AND DISCUSSION

It is impossible to obtain sufficient data to adequately define the model described earlier for any agent. However, we may examine the movement or steady state distribution of a chemical between portions of the model. For example, the distribution of the components of DOWTHERM A between water and air may be re-

$$Air \rightleftarrows Water$$

The vapor pressure of diphenyl and diphenyl oxide is 9.75×10^{-3} and 1.87×10^{-2} mm Hg respectively. Therefore the concentration of these materials, in air at saturation, can be calculated from the gas equation; $n/V = P/RT$. If n/V is expressed as moles/l, P as mm Hg, and T as absolute degrees, R will be 62. For diphenyl, the concentration in saturated air at 25°C will be 5.27×10^{-7} moles/l or 0.081 µg/ml. For diphenyl oxide, the concentration will be 1.0×10^{-6} moles/l or 0.172 µg/ml.

The concentration of diphenyl and diphenyl oxide in water at saturation are 75 and 21 µg/ml. An approximate partition coefficient for diphenyl between water and air accordingly is 75/0.08 or 940. In a similar manner a value for diphenyl oxide is calculated to be 122. Hamaker[12] has recently made the same calculation for a series of pesticides. DP and DPO have values similar to dibromochloropropane and Eptam, respectively, both of which have known volatility properties.

The calculations just presented suggest that DOWTHERM A will be quite readily lost from water to air. The rate of loss will be increased by turbulence. This hypothesis is substantiated by the finding that within 24 hours all of the DOWTHERM A disappeared from a water solution contained in an open shake flask[10] and by the finding of the Waste Control Laboratory.

Available data do not allow much speculation about the distribution of DOWTHERM A between soil and water. The data do indicate that the partitioning of DOWTHERM A between soil and water favors distribution to the soil. Indeed, a portion of the DOWTHERM A may be irreversibly bound to components in the soil.

Using the available information, the effects that may be incurred with a slow leakage of DOWTHERM A into a river or a massive spill of DOWTHERM A into a river may be hypothesized. Assuming

25 lbs/day DOWTHERM A enters a river with a flow rate of 300 cfs. The concentration of DOWTHERM A would be 0.015 ppm, well below the 96 hour no effect level in fish. The concentration would be even lower than this value because partitioning as discussed above would occur. The rate of clearance from the bottom mud will depend on the microflora present. As previously indicated, the metabolism of DOWTHERM A by microflora in the mud may be induced by persistent exposure to DOWTHERM A. Currently, information concerning the fate of DOWTHERM A lost to air is unknown. In conclusion, it is not likely that a leak like that described would have marked untoward effects on the life of the stream.

Will DOWTHERM A bioconcentrate? As indicated in the data section there are suggestions that DOWTHERM A concentrates in fish; however, the reliability of the information is questionable. Even if DOWTHERM A is not metabolized, it would not be expected to biomagnify to the same degree as DDT And PCB. The partition data in Table III indicates that the probability of DOWTHERM A accumulating in the fat of a particular species is much smaller than the probability of DDT and PCB accumulating in fat. In addition to the partitioning factor, the ability of DOWTHERM A to be degraded is much higher than the other two materials. Both of these characteristics will decrease the tendency of diphenyl and diphenyl oxide to accumulate and be magnified in a food chain situation.

TABLE III

Comparison of Partition Data of DOWTHERM A, PCB, and DDT

	Partition Coefficient	Reference
DDT	1×10^6	13
PCB	-1×10^6	14
Diphenyl	1×10^4	Det. by Anal. Lab
Diphenyl Oxide	1×10^4	Det. by Anal. Lab

With regard to a massive spill of DOWTHERM A a concentration gradient running from 100% saturation to almost nothing would be quickly set up. Undoubtedly, aquatic life exposed to concentrations above those listed in Table II would be killed or injured. The rate of dissipation will depend on all of those factors previously mentioned, flow rate of water, partitioning, degradation, etc. In such a situation there will be some death, but an irreversible change in the ecosystem should not occur. This latter statement is supported by Edwards.[16] He claims there is good indications that when aquatic organisms are killed by a large local application of insecticides there is usually a rapid repopulation.

V. CONCLUSIONS AND RECOMMENDATIONS

1. For the situation associated with a slow leak of DOWTHERM A in the range of 25 lbs/day into a stream with a minimam flow of 200 cu ft/sec there should be no adverse effect on the ecosystem.

2. Conditions that exceed these limitations should be examined carefully.

3. Accidental spills of any major chemical should not occur. It is not only bad economics, it is bad ecologically. At best the plant sites should be diked in order that such a spill can be contained and the material dissipated and degraded before allowing it to enter the stream. If such an accident does occur we can only speculate on the effect. If the spill occurs on a major river with a large flow of water the chances of any adverse effect are minimized.

4. We recommend that the predicted movement between air, water, and soil be verified experimentally. This becomes very important as the use of DOWTHERM A incr [illegible]s. We estimate $7,000 for the cost of such a study.

5. The metabolic and accumulation pattern in aquatic species should be investigated and compared with the PCBs. This type of study would be best undertaken with labeled material. The accumu-

cost for an accumulation study is $10,000-12,000.

6. In view of the tendency of this material to enter the air environment a study should be initiated to investigate the rate of degradation by ultra violet light.

7. For the case of a shock load, we will work out the mathematics to characterize the profile of the wave of concentration as it goes down the stream under different initial conditions. This should give us some idea of what shock loads different streams can stand without an adverse effect on the ecosystem.

8. Any research or other plans to produce a derivative of these compounds which is more stable chemically should be examined with a jaundiced eye as it will surely lead to much greater environmental problems.

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